After the numerical integration has been performed, the number of points along each dimension of the grid is doubled and the calculation is repeated. The final result is obtained by extrapolation to $da=0$.

The program *TDS2* is included as a subroutine in our program for applying Lorentz and polarization corrections to intensity measurements. The intensity correction is given by

$$I_{\rm corr}=I_{\rm obs}/(1+\alpha_1-\alpha_1'+\alpha_2-\alpha_2')\ .$$

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On Some Problems Connected with Thermal Motion in Molecular Crystals and a Lattice-Dynamical Interpretation

By Giuseppe Filippini, Carlo M. Gramaccioli, Massimo Simonetta and Giuseppe B. Suffritti

Istituto di Chimica Fisica e Centro C.N.R., Università di Milano, Via Saldini 50, 20133 *Milano, Italy*

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Interpretation of thermal motion in molecular crystals is important for obtaining accurate bond lengths. However, even in a simple case, such as a rigid body, serious difficulties may arise. Contrary to what seems to be a widespread feeling, mathematical methods for overcoming these difficulties, such as regression on principal components, may often lead to results without physical meaning, and a good fit to individual B's is not necessarily a proof of a correct procedure. For an accurate bond-length correction, a lattice-dynamical treatment is particularly promising as a practical method of solution: examples of application, which result in a satisfactory interpretation of molecular motion, are given.

Introduction

For some years, it has been good practice for crystallographers to apply libration corrections to bond distances: for these corrections the molecular motion must be interpreted (Cruickshank, 1956*a*, *b*, *c*, 1961; Busing & Levy, 1964). More recently, the Schomaker–Trueblood approach (Schomaker & Trueblood, 1968) has afforded a complete mathematical method for solving this problem for rigid molecules, and extended discussion of this technique is reported (Johnson, 1970*b*; Pawley, 1970). Among the more noteworthy developments are Pawley's proposal of introducing rigid-body constraints directly into least-squares refinement, with a considerable reduction of the number of parameters to be determined (Pawley, 1964, 1971), and Johnson's 'segmented rigid-body' model (Johnson, 1970*a*).

In the Schomaker–Trueblood treatment, apart from indeterminacy of the trace of **S**, singularity or severe ill-conditioning of the normal-equation matrix may often be encountered; for overcoming some of these difficulties, regression on principal components has been proposed (Johnson, 1970*a*, *b*). We feel that in some cases correct interpretation of thermal motion from diffraction data can be particularly difficult, even for a rigid body, and indiscriminate use of regression on principal components is far from being satisfactory. A detailed discussion about the possibility of obtaining a physically meaningful solution seems to us therefore to be particularly needed.

Regression on principal components

This argument is exhaustively treated in some mathematical and crystallographic works (Golub & Kahan, 1965; Massy, 1965; Kendall & Stuart, 1966; Hanson & Lawson, 1969; Rollett, 1970; Johnson, 1970*b*; Golub & Reinsch, 1970); for our purpose, it is only necessary to keep a few points in mind.

Because of the orthogonality of the latent vectors

$\mathbf{v}_i$ of the **A** matrix, the solution **p** of the normal equations $\mathbf{Ap}=\mathbf{b}$ can always be expressed as a linear combination of the $\mathbf{v}_i$'s:

$$\mathbf{p}=\sum_i s_i\mathbf{v}_i\,. \qquad (1)$$

Pre-multiplying (1) by **A** and knowing that $\mathbf{Av}_i=\lambda_i\mathbf{v}_i$ yields:

$$\mathbf{Ap}=\sum_i s_i\mathbf{Av}_i=\sum_i s_i\lambda_i\mathbf{v}_i=\mathbf{b}\,. \qquad (2)$$

Pre-multiplying (2) by $\mathbf{v}_j^T$ and knowing that $\mathbf{v}_i^T\mathbf{v}_i=\delta_{ij}$, we have:

$$s_i\lambda_i=\mathbf{v}_i^T\mathbf{b}$$

from which:

$$s_i=\mathbf{v}_i^T\mathbf{b}/\lambda_i\,.$$

Pre-multiplying (1) by $\mathbf{v}_j^T$, we have also:

$$s_i=\mathbf{v}_i^T\mathbf{p}\,. \qquad (3)$$

If the matrix **A** is singular, one or more latent roots are zero. If $\lambda_i=0$ and $\mathbf{v}_i^T\mathbf{b}\neq0$, a finite value for the corresponding s_i cannot be obtained and the system is impossible to solve; if $\lambda_i=0$ and $\mathbf{v}_i^T\mathbf{b}=0$, the normal equation system is indetermined and a solution is always obtained for *any* value of s_i. This can be seen in many ways, and for instance it is evident from (2), since the value of **b** is not affected whatever the value of any s_i corresponding to a latent root of zero.

In regression on principal components, all s_i's corresponding to a zero latent root are set to zero; a similar procedure is used when the λ_i's are 'virtually' zero, in

Table 1. *Latent roots for normal-equation matrices for treatment of 'rigid-body' thermal motion*

(*a*) Benzene at −55°C [data from (Bacon *et al.*, 1964): only C atoms considered]

$8{\cdot}5\times10^{-5}$	1·862	2·355	2·785	4·932	6·000	6·000
7·508	14·88	15·43	17·31	29·22		

(*b*) Diethyl ether 1st molecule (André *et al.*, 1972)

0·0	$1{\cdot}5\times10^{-6}$	0·580	1·231	1·248	1·976	2·077
2·306	4·131	5·000	5·000	5·276	7·247	14·04
17·81	29·41	57·52	59·44	71·92	74·00	74·09

(*c*) Diethyl ether 2nd molecule (André *et al.*, 1972)

0·0	$8{\cdot}7\times10^{-6}$	0·590	1·199	1·268	1·915	2·146
2·296	4·128	5·000	5·000	5·278	7·246	13·88
17·64	29·06	56·83	58·70	69·98	72·04	72·13

(*d*) Anthracene [data from R. Mason in Lonsdale & Milledge (1961)]

1·728	6·433	6·951	11·18	14·00	14·00	21·42
93·82	223·4	759·8	1020·0	1282·0		

Table 2. *Latent vectors (normalized) for 'nearly zero' latent roots of normal-equation matrices*

Here, the Cartesian reference system has been taken as coincident with the crystallographic axes.

	Benzene (−55°C)	Diethyl ether (1st)		Diethyl ether (2nd)	
Latent root	$8{\cdot}5\times10^{-5}$	0·00	$1{\cdot}5\times10^{-6}$	0·00	$8{\cdot}7\times10^{-6}$
T_{11}	0·446	0·00	−0·134	0·00	−0·131
T_{22}	0·052	0·00	0·00	0·00	0·00
T_{33}	0·421	0·00	0·00	0·00	0·00
T_{12}	0·152	0·00	0·003	0·00	−0·005
T_{13}	0·433	0·00	0·00	0·00	−0·002
T_{23}	0·147	0·00	0·00	0·00	0·00
L_{11}	−0·246	0·00	0·00	0·00	0·00
L_{22}	−0·448	0·00	−0·018	0·00	−0·019
L_{33}	−0·257	0·00	0·985	0·00	0·985
L_{12}	0·081	0·00	0·001	0·00	−0·002
L_{13}	0·224	0·00	−0·002	0·00	−0·009
L_{23}	0·073	0·00	−0·001	0·00	0·00
S_{11}		0·577	−0·001	0·577	−0·003
S_{22}		0·577	0·001	0·577	0·005
S_{33}		0·577	−0·001	0·577	−0·002
S_{12}		0·00	0·00	0·00	0·00
S_{13}		0·00	0·00	0·00	0·00
S_{23}		0·00	0·00	0·00	0·00
S_{21}		0·00	0·00	0·00	−0·001
S_{31}		0·00	−0·110	0·00	−0·111
S_{32}		0·00	−0·002	0·00	0·004

order to eliminate several kinds of ill-conditioning (Rollett, 1970).

The Schomaker–Trueblood treatment (including **S**) always leads to a normal-equation matrix with at least one latent root equal to zero; the relative latent vector has all its components equal to zero, except those corresponding to S_{11}, S_{22} and S_{33}, where (if normalized) they are all equal to $1/\sqrt{3}$.* This happens because the trace of **S** is indetermined. From (3), and considering the nature of this latent vector, we see that assigning $s_i=0$ in this case means choosing the solution corresponding to $\mathrm{Tr(S)}=0$, as suggested by Schomaker & Trueblood.

Our solution is however somewhat arbitrary, the values of the diagonal elements of **S** being essentially deduced on the basis of an assumption without physical grounds. Except for particular cases connected with crystallographic molecular symmetry, there is in fact no reason why Tr(S) should be zero and this can be seen when one considers results of lattice-dynamical calculations (Table 6).

To most crystallographers, the exact knowledge of **S** (and **T**) tensors is not essential because librational corrections for bond lengths in rigid molecules depend only on the value of **L** and for this reason regression on principal components can be safely applied to many cases. However, it is important to be sure that no indeterminacy involves any component of **L**; otherwise we have meaningless bond-length corrections. For this reason, it is essentially to examine all latent vectors whose λ_i is zero or nearly so: *all these vectors should have negligible components relative to any* L_{ij}.

Some practical cases

A notable example is benzene, one of the first substances whose bond lengths, as determined by X-ray diffraction, were corrected for thermal libration (Cox, Cruickshank & Smith, 1958).

As shown in the original paper, a rigid-body analysis limited to carbon atoms leads to an indeterminate result; this happens because the atoms lie on a conic section (Johnson, 1970*b*). Examination of the latent roots of the normal-equation matrix (Table 1) and the latent vector corresponding to the zero λ_i (Table 2)† makes it evident that indeterminacy involves **L**. This shows the impossibility of obtaining corrections for thermal libration, unless some additional assumptions are made. Reasonable assumptions have indeed been made by Cox, Cruickshank & Smith for their study of benzene and presumable by Bacon, Curry & Wilson (1964) in a neutron diffraction study of the same substance.

Application of regression on principal components leads to the **T** and **L** tensors reported in Table 3; here these tensors are compared with another possible solution, obtained by assigning to s_i the value 0·03 instead of zero. In spite of the essential differences between both sets of **T** and **L** tensors, the fit to experimental **B**'s is practically the same (Table 4); it would have been identical if λ_i were exactly equal to zero. If introduction of hydrogen atoms with their thermal factors, as derived from neutron diffraction indeed leads to the 'true' solution, this also is completely different from results obtained from regression on principal components (Tables 3, 4).‡

Table 3. *Comparison of various sets of* **T**, **L** *tensors which fit the experimental* **B**'s *for benzene* (*see text*)

	$s_i=0$ (regression on p.c.)	$s_i=0\cdot03$	With H atoms
T_{11}	0·020	0·033	0·027
T_{22}	0·039	0·040	0·040
T_{33}	0·030	0·043	0·041
T_{12}	−0·005	−0·007	−0·002
T_{13}	−0·012	0·012	−0·014
T_{23}	−0·007	−0·003	−0·007
L_{11}	0·012	0·005	0·009
L_{22}	0·022	0·008	0·013
L_{33}	0·011	0·003	0·012
L_{12}	−0·001	0·001	−0·002
L_{13}	−0·004	0·003	−0·002
L_{23}	−0·002	−0·001	−0·002

Table 4. *Comparison between observed* **B**'*s for benzene at* −55°C *and calculated values corresponding to various sets of* **T**, **L** *tensors as reported in Table* 3 ($\text{Å}^2\times10^4$)

Atom		Experimental	$s_i=0$	$s_i=0\cdot03$	With H atoms
C(1)	B_{11}	143	139	139	173
	B_{22}	87	89	89	92
	B_{33}	227	221	221	237
	B_{12}	−8	3	3	14
	B_{13}	−15	−15	−15	−38
	B_{23}	−18	−11	−11	−16
C(2)	B_{11}	136	143	143	144
	B_{22}	110	113	113	123
	B_{33}	227	218	218	220
	B_{12}	11	4	4	16
	B_{13}	27	32	32	−9
	B_{23}	−12	−19	−18	−20
C(3)	B_{11}	153	150	150	156
	B_{22}	108	104	104	109
	B_{33}	186	200	200	222
	B_{12}	−11	−15	−15	−13
	B_{13}	15	9	9	−21
	B_{23}	6	6	6	3

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* This reasoning is strictly valid when no degeneracy occurs for $\lambda=0$, *i.e.* no other latent root is zero, as for most cases where the Schomaker–Trueblood treatment is actually useful.

† A 'complete' Schomaker–Trueblood treatment involving **S** leads to a matrix with *two* λ_i's close to zero. Here the molecule is in a centrosymmetric position and, since $\mathbf{S}=0$, this tensor can be omitted from our treatment, which becomes identical with that of Cruickshank (1956).

‡ The results can be somewhat improved if the contribution of internal motion is subtracted (Johnson, 1970*a*; Bacon, Curry & Wilson, 1964). This contribution is small, being quite negligible for carbon atoms and of the order of about 10% for hydrogen atoms. For this reason, we have omitted it from our calculations, which were performed in this case merely to show the large differences between different interpretations.

A similar case occurs for diethyl ether (André, Fourme & Zechmeister, 1972). Here regression on principal components was used in order to eliminate the difficulties due to a severe ill-conditioning of the normal-equation matrix. However (Table 2), for each independent molecule one of the two latent vectors corresponding to a zero λ_i involves components of **L** (especially L_{33}); for this reason, unless some well founded assumptions are made, the results as reported appear very questionable as far as bond length corrections are concerned (apart from the objection that is difficult to imagine a molecule of this kind to be rigid).

Table 5. *Experimental* (*obs.*) *and 'dynamical'* (*cal.*) *values of anisotropic temperature factors* (×10⁴)†

The temperature factors are in the form:

$$T_i = \exp\,[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$$

	B_{11}		B_{22}		B_{33}		B_{12}		B_{13}		B_{23}	
	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.
ANT = anthracene (Mason, 1964; Lonsdale & Milledge, 1961)												
A	271	291	444	482	136	136	6	34	112	111	−22	1
B	197	254	217	364	116	131	−10	4	73	90	−23	−29
C	150	174	242	270	124	123	−2	2	73	70	−1	−11
D	158	183	241	249	130	134	−5	−15	77	74	−31	−12
E	144	168	241	267	126	129	−11	0	72	74	21	4
F	189	227	332	351	146	157	15	−5	85	104	−31	33
G	260	271	468	473	144	155	16	27	114	122	61	46
BCP = benzo[*c*]phenanthrene (Hirshfeld, Sandler & Schmidt, 1963)												
C(1)	38	37	34	33	237	269	−4	−1	10	−3	−6	−8
C(2)	46	48	41	41	338	340	−7	2	13	8	−25	−27
C(3)	71	66	45	44	262	308	−11	−4	25	14	−19	−28
C(4)	77	68	44	43	237	248	−19	−11	−10	−10	9	−7
C(5)	61	51	53	52	354	307	−15	−12	−80	−43	49	31
C(6)	40	39	58	56	382	373	−6	−6	−41	−32	58	44
C(7)	36	34	32	31	200	220	−5	−5	−8	−4	25	13
C(8)	52	49	39	38	210	234	−16	−10	−25	−17	30	15
C(9)	33	34	35	31	238	229	−1	−2	5	2	33	24
C(10)	32	34	47	43	353	311	−2	−1	−12	−2	46	40
C′(1)	40	41	35	34	317	285	−3	−4	2	1	−21	−12
C′(2)	58	57	42	43	399	352	−3	−7	−34	−11	−34	−33
C′(3)	97	78	44	44	393	323	5	−1	−34	−2	−43	−33
C′(4)	77	74	47	41	321	288	14	7	19	27	−19	−8
C′(5)	48	49	48	49	426	365	13	11	61	44	39	32
C′(6)	36	39	53	55	460	408	11	7	24	23	58	45
C′(7)	37	39	32	30	232	234	0	0	5	9	15	12
C′(8)	48	52	36	36	299	270	10	6	29	27	26	15
BIC = bicyclo[2,2,2]octene-2,3-*endo*-dicarboxylic anhydride (Destro, Filippini, Gramaccioli & Simonetta, 1971)												
C(1)	193	186	67	76	61	68	32	28	3	10	3	1
C(2)	183	201	69	88	43	54	−5	20	12	12	−11	−10
C(3)	162	179	72	83	42	59	−2	19	−7	−3	−4	−2
C(4)	181	206	75	74	53	69	21	25	27	31	6	1
C(5)	303	204	64	67	40	51	4	8	6	12	−4	−4
C(6)	251	229	78	82	46	57	−17	−5	−15	−15	6	6
C(7)	291	270	59	60	75	90	5	15	18	21	5	2
C(8)	244	232	92	80	69	94	−26	−6	33	40	12	7
C(9)	201	245	104	131	48	63	−23	9	10	33	−4	13
C(10)	228	280	87	91	48	66	10	34	−1	−1	12	17
O(1)	256	324	88	116	68	67	−16	−2	24	17	18	29
O(2)	215	288	165	203	111	101	−6	12	54	78	13	30
O(3)	363	407	92	103	110	103	61	80	29	7	31	32
BNZ = benzene at −135 °C (Bacon *et al.*, 1964)												
C(1)	83	154	49	74	111	174	3	1	−12	−7	0	−2
C(2)	83	147	56	92	119	171	−3	1	20	20	−3	−5
C(3)	94	153	51	84	128	161	0	−15	0	5	3	9
H(1)	184	243	69	77	204	268	0	15	20	4	6	1
H(2)	174	222	134	135	243	257	40	27	114	89	31	−9
H(3)	177	227	98	116	221	233	−11	−27	55	49	46	39

† Data for naphthalene, phenanthrene and pyrene have been reported elsewhere (Filippini, Gramaccioli, Simonetta & Suffritti, 1973).

Table 5 (*cont.*)

	B_{11}		B_{22}		B_{33}		B_{12}		B_{13}		B_{23}	
BUT = 1,6:8,13-butane-1,4-diylidene [14] annulene (Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1972)												
	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.
C(1)	30	25	49	52	168	153	0	0	0	0	6	3
C(2)	26	22	61	60	157	140	−7	−5	−4	−2	−9	−1
C(3)	30	24	92	84	231	198	−17	−12	−4	2	21	9
C(4)	23	20	138	117	253	224	−12	−8	7	6	9	6
C(5)	22	21	74	67	148	122	0	0	−9	−7	0	−1
C(6)	36	28	86	81	113	107	0	0	−10	−7	0	−1
DTO = 3,4:7,8-dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene (Barnett & Davis, 1970)												
C(1)	70	52	93	90	170	146	1	4	−5	3	−3	2
C(2)	67	50	103	108	144	155	2	6	−3	2	6	5
C(3)	79	51	160	158	178	201	10	14	1	4	−3	−3
C(4)	62	50	216	182	207	223	3	2	−1	−6	16	11
C(5)	72	59	158	167	183	207	−4	−9	−13	−20	4	−1
C(6)	82	63	139	149	156	168	2	−3	−10	−14	−11	−16
C(7)	63	54	114	112	152	137	3	0	−1	−1	8	3
C(8)	62	52	124	107	143	126	2	1	3	6	0	6
PAN = 1,6:8,13-propane-1,3-diylidene[14]annulene (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972)												
C(1)	38	30	6	5	153	195	0	1	−13	−4	7	4
C(2)	48	34	9	7	225	253	2	2	−30	−23	9	6
C(3)	32	29	10	8	370	369	1	3	−36	−27	0	1
C(4)	28	22	10	9	388	398	1	2	7	1	1	−1
C(5)	29	23	10	8	297	300	3	1	24	20	7	3
C(6)	30	24	7	6	144	191	1	1	14	13	−2	1
C(7)	33	27	7	6	129	181	0	0	11	6	7	7
C(8)	33	26	6	5	164	191	0	0	−12	−6	2	1
C(9)	34	28	8	6	257	308	−1	1	−19	−22	7	5
C(10)	32	23	8	7	404	438	0	1	−31	−21	−5	−5
C(11)	27	21	8	8	444	445	−1	−1	10	10	−10	−12
C(12)	29	25	10	8	317	319	−4	−3	17	26	−2	−7
C(13)	30	26	5	5	225	217	−2	−2	12	12	1	−1
C(14)	39	31	8	6	191	177	−2	−2	22	9	4	4
C(15)	34	28	5	5	240	218	3	2	−2	3	−3	−4
C(16)	41	33	5	5	225	249	1	1	−9	−3	−4	−10
C(17)	32	26	6	4	190	217	−1	−1	−9	−3	−9	−5

Although benzene and diethyl ether are examples of a singular matrix of the normal equations (apart from the indeterminacy of **S**) a certain degree of ill-conditioning seems to occur for many 'rigid' molecules. For instance, the latent roots of the corresponding matrix for anthracene range from 1·7 to 1282. Although this is not strictly a measure of ill-conditioning, it has something in common with other more serious cases, the smallest latent roots being about two orders of magnitude below the average (Table 1).

In our opinion, this is the reason why a lattice-dynamical interpretation (see below) leads to **B**'s much closer to observed values (13 %), whereas considerable differences can be observed between 'dynamical' and 'crystallographic' **T**, **L** tensors (see especially L_{33} in Table 6).

This means that a very different interpretation in terms of **T**, **L** can be obtained for only slightly different values of temperature factors, usually well within their real accuracy. An obvious consequence is that, since the accuracy of the **B**'s is generally rather low, for some molecules application of a rigid-body fit to the observed temperature factors results in such a poorly defined **L** tensor as to cause significant uncertainties in bond lengths (Table 7).* This should be taken into account when accuracies below 0·005 Å are claimed.

Lattice-dynamical interpretation

For all these reasons, the problem of a general treatment of a libration correction for bond lengths is of doubtful validity even for rigid bodies: as we have seen, the major difficulties occur when molecules are small or highly symmetric. Moreover, a general treatment of a non-rigid movement needs data, such as mutual correlations, which cannot be obtained from X-ray or neutron diffraction (Busing & Levy, 1964; Johnson, 1970*a*) and often even a simplified analysis, such as

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* Although Table 7 shows a comparison between 'crystallographic' and 'dynamical' bond-length corrections for thermal motion, since the discrepancy between the **L** tensors is practically within experimental error, the example is meaningful also for this purpose.

Table 6. **T**, **L**, **S** *tensors*: (1) *from the Schomaker–Trueblood treatment*; (2) *from our dynamical calculations*†

Cartesian reference system with axes on **a***, **b**, **a*** × **b**.

		T (Å^2 × 10^4)			**L** (rad^2 × 10^4)			**S** (Å rad × 10^4)			Lat. roots of **L** (deg^2)
ANT											
	(1)	391	27	−93	23	0	1				10·0
			423	−25		24	0				8·0
				500			18				3·3
	(2)	444	15	−101	33	0	−5				19·2
			442	−15		26	−12				10·6
				514			53				6·9
BCP											
	(1)	342	−36	−2	16	−2	1	−6	3	19	17·4
			325	103		53	2	−8	37	13	7·4
				363			23	−14	−15	−32	5·2
	(2)	366	−24	9	15	0	−2	2	3	7	12·9
			301	80		37	5	−1	26	9	8·6
				376			28	−9	−14	−30	4·8
BIC											
	(1)	331	−4	−32	55	−8	7	7	−24	−2	32·8
			312	−34		71	−25	−15	−8	10	17·2
				279			73	18	−5	0	15·2
	(2)	329	32	−19	46	−3	−1	−2	−47	5	29·4
			339	−6		64	−19	10	14	−2	17·4
				345			61	33	−18	−10	15·5
BNZ											
	(1)	117	−62	−67	57	−23	−9				45·4
			219	−29		123	−27				24·4
				177			73				13·0
	(2)	322	−34	−32	52	−3	−5				30·6
			322	−15		88	−13				19·7
				305			61				15·7
BUT											
	(1)	372	0	0	41	0	0	0	−4	0	15·5
			323	0		22	0	16	0	0	13·4
				201			47	0	0	0	7·3
	(2)	319	0	0	32	0	0	0	1	0	11·1
			341	0		18	0	9	0	0	10·5
				188			34	0	0	0	5·9
DTO											
	(1)	387	2	−37	39	−1	22				18·5
			283	16		7	−1				3·9
				312			29				2·3
	(2)	284	4	−20	43	0	18				17·8
			263	14		13	−1				4·7
				283			25				4·1
PAN											
	(1)	554	−14	13	65	−5	9	−15	−8	20	22·3
			314	6		51	5	5	14	−10	16·8
				276			24	−32	−7	2	6·9
	(2)	436	−3	27	58	0	9	−13	−8	6	19·8
			250	−10		43	5	2	5	−7	14·4
				350			25	−29	4	−8	7·1

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† Data for naphthalene, phenanthrene and pyrene have been reported elsewhere (Filippini, Gramaccioli, Simonetta & Suffritti, 1973).

Johnson's 'segmented rigid-body' is difficult to apply in practice.[†]

An application of lattice dynamics to these crystallographic problems seems promising, especially in view of some results already obtained (Cochran & Pawley, 1964; Pawley, 1967, 1972; Cerrini & Pawley, 1973; Filippini, Gramaccioli, Simonetta & Suffritti, 1973; Gramaccioli, Simonetta & Suffritti, 1973; Scheringer, 1973). Lattice dynamics provides a way of checking consistency of thermal-motion interpretation with other kinds of experimental evidence, such as Raman or infrared spectra, a point which cannot be treated if only a fit of **B**'s is available. For this reason, we started a series of calculations mainly on structures of 'rigid' hydrocarbons, for which accurate data are known. This kind of substance was chosen as the first to be tested, because reasonable functions for packing energy are available and only computer programs of moderate complexity are necessary.

In most cases, a fair to excellent agreement between observed and calculated **B**'s was found (Table 5), confirming the validity of this lattice-dynamical procedure. The agreement between 'dynamical' and 'crystallographic' **T**, **L**, **S** tensors is apparently less good and is shown in Table 6; the reason why this happens has already been given for anthracene (see above) and is more or less the same for the other substances, where the situation is, however, not so critical. Because of these differences, bond-length corrections are not exactly the same for the crystallographic and dynamical interpretations, in some cases (as for anthracene) involving variations up to 0·004 Å (see Table 7 for some examples).

At least for some substances, such as anthracene or even benzene at low temperature,[‡] we think that the dynamical results may actually be the more reliable, in spite of the approximations involved in their derivation, because of the satisfactory (often excellent) agreement with spectroscopic data and experimental dispersion curves (Taddei, Bonadeo, Marzocchi & Califano, 1973; Filippini, Gramaccioli, Simonetta & Suffritti, 1973; Lutz & Halg, 1970).

The procedure adopted in our calculations is similar to Pawley's routine (Pawley, 1967, 1968, 1972). The essential difference consists in sampling the Brillouin zone, a point which is particularly important for obtaining physically significant values of the tensor **T** (Gramaccioli, Simonetta & Suffritti, 1973). In these calculations, various empirical functions have been considered, in most cases with essentially similar results; the best agreement with experimental data has been obtained by use of some functions proposed by Williams (1967) and the results here reported refer only to these functions, which are used without modifications for all substances here treated.

The calculations, although complicated, can be reduced to a matter of routine, if appropriate computer programs are available: a more detailed description of our programs is given elsewhere (Filippini, Gramaccioli, Simonetta & Suffritti, 1973). The only input con-

Table 7. *Bond lengths corrected for rigid-body motion*: (1) *from the Schomaker–Trueblood treatment*, (2) *from our dynamical calculations*

ANT

	(1)	(2)
A–B	1·376	1·377
B–C	1·447	1·448
C–D	1·412	1·413
C–E′	1·426	1·430
D–E	1·403	1·404
E–F	1·442	1·443
F–G	1·362	1·364
A–G′	1·414	1·417

BUT

	(1)	(2)
C(1)—C(2)	1·428	1·427
C(1)—C(15)	1·511	1·510
C(1)—C(14)	1·402	1·401
C(2)—C(3)	1·368	1·366
C(4)—C(3)	1·424	1·423
C(15)–C(16)	1·523	1·522
C(16)–C(17)	1·525	1·523

PAN

	(1)	(2)
C(1)—C(2)	1·416	1·415
C(1)—C(14)	1·396	1·396
C(1)—C(15)	1·509	1·507
C(2)—C(3)	1·389	1·389
C(3)—C(4)	1·416	1·415
C(4)—C(5)	1·383	1·383
C(5)—C(6)	1·417	1·416
C(6)—C(7)	1·386	1·385
C(6)—C(15)	1·514	1·513
C(7)—C(8)	1·393	1·393
C(8)—C(9)	1·413	1·412
C(8)—C(17)	1·530	1·529
C(9)—C(10)	1·396	1·395
C(10)–C(11)	1·412	1·411
C(11)–C(12)	1·381	1·380
C(12)–C(13)	1·407	1·407
C(13)–C(14)	1·405	1·404
C(13)–C(17)	1·516	1·515
C(15)–C(16)	1·520	1·519
C(16)–C(17)	1·515	1·515

[†] In Johnson's (1970*a*) procedure, it is not clear how he modifies the model to eliminate the dependent linear combinations of variables: it seems that regression on principal components is applied for this purpose (see especially p. 157). However, since this method alone may not afford a physically valid solution in all cases, it is not easy to make the necessary assumptions for each substance

[‡] Temperature factors for benzene at low temperature are not so accurate as for the other structures here considered, because an incomplete set of data has been used and, moreover, scale factors between the various layers have apparently been adjusted during some cycles of the refinement (Bacon *et al.*, 1964). This might be a reason for the rather poor agreement between experimental and calculated **B**'s even at low temperature, while the agreement with experimental vibration frequencies is good (Taddei, Bonadeo, Marzocchi & Califano, 1973): in this work, benzene has been considered mainly to show a critical case in evaluating **T** and **L**.

sists of cell parameters, experimental atomic coordinates, space-group symmetry operations, maximum packing distance (here 5·50 Å) and empirical packing-energy functions. Computing time is of the order of 20 min on a medium-fast computer such as UNIVAC 1106.

Limits and further developments

In order to extend the lattice-dynamical treatment to other organic molecules, a prime need is reliable empirical functions for non-bonded energy. At present, 'good' functions are known mainly for hydrocarbons, and application to nitrogen or oxygen-containing molecules is still rather awkward; however BIC is reported in Table 6 and the agreement with experimental **B**'s is good. In this case, interaction energy involving oxygen has been evaluated with a formula proposed by Kitaigorodskii (1961), where the van der Waals radii for oxygen, carbon and hydrogen were assumed to be 1·5, 1·7 and 1·5 Å respectively.

Some difficulties also arise when molecular movements are too large and become clearly incompatible with a harmonic treatment. A case of this kind is particularly evident in Table 8, where the agreement between observed and calculated temperature factors for benzene is reported as a function of temperature. For this molecule, the root-mean-square amplitudes of molecular motions can be very large (up to 8° and 0·23 Å) and this definitely compromises our results when the temperature is higher than about −135°C.

Table 8. *Agreement between observed and 'dynamical'* **B**'*s for benzene as a function of temperature*

The experimental r.m.s. amplitudes of thermal motion are also reported.

			R.m.s. amplitudes (only C atoms)	
	R*	ΔB†	Translational	Rotational
−3°C	0·77	−0·72	0·23 Å	7·9°
−55°C	0·48	−0·39	0·19	4·9
−135°C	0·34	−0·22	0·15	2·5

* $R=\sum|B_{\text{obs}}-B_{\text{dyn}}|/\sum|B_{\text{obs}}|$.
† $\Delta B=\sum(B_{\text{obs}}-B_{\text{dyn}})/\sum|B_{\text{obs}}|$.

Another point to be developed is application to 'segmented rigid' molecules and a computer program for this purpose is at present being written in this labatory. The 'complete' dynamical problem of treatmenort of a non-rigid molecule can also be handled, although at present the large size of dynamical matrices is a serious obstacle for a routine application.

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